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STUDIES ON THERMOCHEMICAL
WATER-SPLITTING CYCLES

Final Report

by

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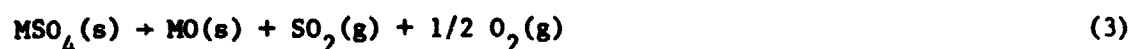
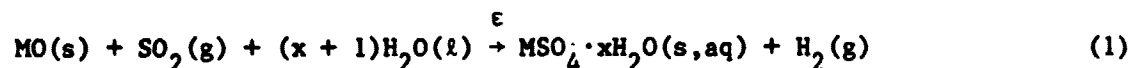
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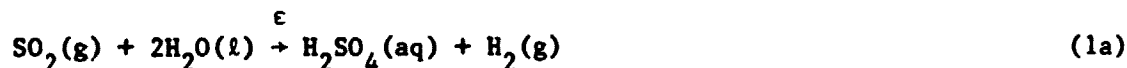
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ABSTRACT

The higher temperatures and more nearly isothermal heat profiles of solar (and, possibly, nuclear fusion) heat sources demand that new cycles (as opposed to the cycles already developed for PTR's) be developed to realize the full potential of these newer heat-source technologies. The metal oxide-metal sulfate class of cycles under development at IGT appear well suited for solar heat sources. This class of cycles may be represented by Reactions 1 through 3, where M indicates a metal or reduced metal oxide species.



Reaction 1 may be written as the sum of Reactions 1a and 1b, where Reaction 1a is the electrochemical oxidation of SO_2 and Reaction 1b is a thermochemical reaction.



The cell voltage at workable current densities required for the oxidation of SO_2 (Reaction 1a) is critical to the efficient operation of any metal oxide-metal sulfate cycle. The key to making a practical sulfur dioxide depolarized electrolysis cell for the splitting of water is the optimization of the anode reaction.

The electrolytic oxidation of sulfur dioxide to produce sulfuric acid and hydrogen has been studied extensively in conjunction with the WAES sulfur cycle. These studies, however, have been limited to sulfuric acid concentrations of 50 weight percent or more because of the need to produce concentrated acid in that cycle. Metal oxide-metal sulfate cycles do not require the production of concentrated sulfuric acid. The purpose of this program is to examine the electrolytic oxidation of sulfur dioxide in dilute sulfuric acid solutions that are appropriate for metal oxide-metal sulfate cycles and to determine preferred cell operating conditions.

SUMMARY

The purpose of this program was to assess the electrochemical oxidation of sulfur dioxide in relatively dilute (less than 50 weight percent) sulfuric acid and to determine the preferred operating conditions (acid concentration, temperature, electrode materials) for such a cell to be mated with a metal oxide-metal sulfate water-splitting cycle. Our rough performance goals were 200 mA/cm^2 at 0.5 V.

The choice of the best sulfuric acid concentration is not straightforward due to the following multiple, often opposite, effects:

- Cathode performance is best at high acid concentrations.
- Anode performance increases markedly as acid concentration is reduced from 50 to 33 weight percent and is relatively insensitive to further reductions in concentration.
- Electrolyte resistivity, which will be directly proportional to cell IR losses, is at a minimum at sulfuric acid concentrations of about 30 to 35 weight percent.

Considering all of these factors, (anode performance and solution resistivity appear most critical), we conclude that sulfuric acid concentrations of 30 to 35 weight percent are preferred, and selected 33 weight percent as the common basis for further experiments.

Temperature effects are relatively straightforward. All other factors being equal, both anode and cathode performances increased across the temperature range investigated (0° to 75°C). Higher partial pressures of SO_2 at the anode will be necessary at high temperatures to maintain SO_2 activity. Temperatures of 75°C or higher are preferred.

None of the anode materials tested performed as well as the two platinum-based materials (smooth and platinized platinum). We certainly did not make a comprehensive materials survey, but platinized platinum or smooth platinum gave the best anode kinetics at a given potential of the five materials examined.

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Cell performance in relatively dilute sulfuric acid is better than the performance of a similarly designed cell at acid concentrations of 50 weight percent or above. However, even at the best conditions tested in this program (33 weight percent sulfuric acid, 75°C, platinum anode and cathode, anode saturated with sulfur dioxide at 1 atm pressure), we did not achieve the performance goals of 200 mA/cm² at 0.5 V or less.

On the other hand, the use of a homogeneous catalyst such as iodine to replace the anode mechanism does hold promise of meeting the above performance goals with cheap (relative to noble metals) anode materials. The limited number of experiments using homogeneous catalysis yielded a current density of 100 mA/cm² at an anode potential of 450 mV RHE on crude porous carbon electrodes at 25°C in 33 weight percent acid. This translates to a total voltage of approximately 600 mV in a properly constructed cell. Factors (untested at present) that would tend to increase this measured performance are higher temperatures, higher SO₂ pressures, and more sophisticated methods for anode fabrication. There is every reason to believe that cell performance goals of 200 mA/cm² at 0.5 V can be achieved or exceeded on cheap electrode materials with proper cell development.

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INTRODUCTION

Background Discussion

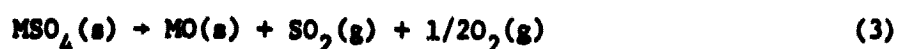
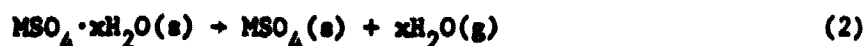
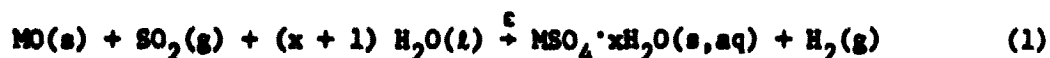
The larger part of early thermochemical water-splitting development has been aimed at interfacing the endothermic reaction steps with the secondary helium-coolant streams of high-temperature nuclear fission reactors (HTR's). At present, the attainable upper temperature for such coolant streams is about 1150 K, limiting the energy efficiency of a process to a second-law efficiency (Carnot function) of less than 0.69. For nonisothermal process heat temperatures available from solar concentrators, which are in the range of 1500 to 2500 K, the second-law efficiency limitations range from 0.78 to 0.86.

There is also a basic difficulty in mating processes to a nuclear fission reactor energy source (HTR). Thermochemical processes absorb heat isothermally for high-temperature endothermic reactions and reject heat at low temperatures. HTF's offer high-temperature interfacing capability of severely limited capacity. The temperatures of the secondary heat-exchange loops (usually helium-filled) are high enough for many cycles, but the capacity for transfer of heat is low; large amounts of heat are delivered only with the concomitant penalty of downward cascading temperatures. Supply of heat at several decreasing temperatures calls for a cycle with several isothermal heat requirements rather than one requirement at high temperature. Such cycles are inherently less efficient than cycles with fewer reaction sequences.

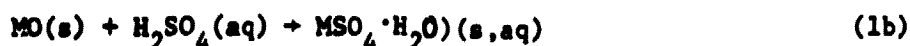
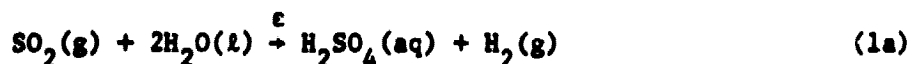
Solar concentration sources also are capacity-limited, but through engineering design they are expected to be capable of yielding near-isothermal heat at higher temperatures than HTR's. The upper limit for certain types of solar concentrators appears to be 2000 K, and isothermal heat at temperatures as high as 1600 to 1800 K may be available during periods of insolation. In the longer term, some nuclear fusion designs project the availability of nearly isothermal heat at equally attractive temperatures.

The higher temperatures and more nearly isothermal heat profiles of solar (and, possibly, nuclear fusion) heat sources demand that new cycles (as opposed to the cycles already developed for HTR's) be developed to realize the full potential of these newer heat-source technologies. The metal oxide-metal sulfate class of cycles under development at IGT appear well suited

for solar heat sources. This class of cycles may be represented by Reactions 1 through 3, where M indicates a metal or reduced metal oxide species.



Reaction 1 may be written as the sum of Reactions 1a and 1b, where Reaction 1a is the electrochemical oxidation of SO_2 and Reaction 1b is a thermochemical reaction.



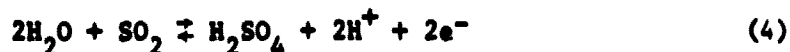
The most-developed hybrid cycle, the sulfur cycle developed by Westinghouse Alternative Energy Systems Division (WAES), involves Reaction 1a and the subsequent concentration and thermal decomposition of sulfuric acid using a high-temperature nuclear (HTR) heat source. The metal oxide-metal sulfate cycles offer the following potential advantages over the sulfur cycle:

- The concentration of sulfuric acid by boiling is eliminated. This boiler is expensive in terms of both the amount of heat required and the materials of construction needed for boiling acid. In metal oxide-metal sulfate cycles, solid metal sulfate is used to "concentrate" the sulfate produced electrochemically.
- The need to produce concentrated (greater than 50 weight percent) sulfuric acid is eliminated. This allows improvement in the electrochemical step because anodic overpotentials increase as the acid concentration increases, and the conductivity of the solution decreases at acid concentrations above about 30% to 35%, which increases internal resistance (IR) losses.
- Primary heat requirements for metal oxide-metal sulfate cycles are primarily isothermal and high temperature, which allows these cycles to take better advantage of the capabilities of high-temperature solar heat sources.

The cell voltage at workable current densities required for the oxidation of SO_2 (Reaction 1a) is critical to the efficient operation of any metal oxide/metal sulfate cycle. The key to making a practical sulfur dioxide depolarized electrolysis cell for the splitting of water is the optimization of the anode reaction. Thermochemical calculations for the electrolysis of water in the presence of sulfur dioxide to form sulfuric acid

and hydrogen (Reaction 1a) yield an equilibrium cell voltage of 170 mV when all chemical species are present at unit activity.³

This, in turn, dictates an anode potential for the half-cell reaction (Reaction 4) of +170 mV,

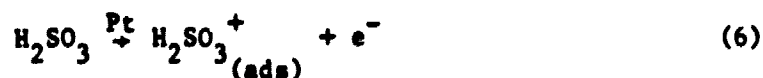


because under these conditions the cathode can be viewed as a reversible hydrogen electrode (RHE) (Reaction 5).

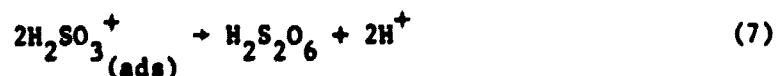


If reasonable estimates for overpotential and IR losses are added to the equilibrium cell voltage (for example, 100 mV overpotential at each electrode and 100 mV IR loss through the electrolyte), a cell voltage of about 470 mV can be projected for a practical cell operating at a useful rate. However, under actual experimental conditions, the half-cell potential for the anodic reaction is on the order of +400 mV versus RHE, and appreciable rates of reaction can only be achieved at cell voltages above 800 mV.

The reason for this behavior is not clear, but recent work by A. J. Appleby and B. Pichon¹ on the mechanism of the SO_2 reaction has shed considerable light on the problem. They have suggested a three-step mechanism for the oxidation of sulfur dioxide on platinum. The first step involves the adsorption of hydrogen sulfite (or water and sulfur dioxide) onto the platinum surface with simultaneous electron transfer of one electron to the anode:



The second step combines two H_2SO_3^+ ions on the surface to form dithionic acid and two hydronium ions:

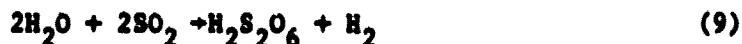


This step is rate determining. Finally, the dithionic acid disproportionates to sulfuric acid and sulfur dioxide:



Appleby and Pichon¹ are quick to point out that this mechanism is not proven and at present only stands as a working hypothesis. If their mechanism is

correct, however, then thermochemical calculations of cell voltage based upon Reaction 1a are incorrect. The equation for the electrochemistry of the cell reaction should be—



with a thermochemically calculated equilibrium cell voltage³ of 570 mV. The fact that dithionic acid is unstable at a pH less than one explains the formation of sulfuric acid via Reaction 8 as a final product. If this is true, then a practical operating cell voltage below 800 mV will be exceedingly difficult to achieve without a catalyst for the rapid decomposition of dithionic acid.

This fact was not immediately obvious at the beginning of this program; as the task work proceeded the need for an additional series of experiments aimed at altering the reaction mechanism became apparent. Therefore, we performed a series of experiments in which iodide ion was added to the anolyte. The experimental results of this and all other task work are reported and discussed in this report.

Program Scope

The electrolytic oxidation of sulfur dioxide to produce sulfuric acid and hydrogen has been studied extensively in conjunction with the WAES sulfur cycle. These studies, however, have been limited to sulfuric acid concentrations of 50 weight percent or more because of the need to produce concentrated acid in that cycle. As noted in the previous section, metal oxide-metal sulfate cycles do not require the production of concentrated sulfuric acid. The purpose of this program is to examine the electrolytic oxidation of sulfur dioxide in dilute sulfuric acid solutions that are appropriate for metal oxide-metal sulfate cycles and to determine preferred cell operating conditions.

Task 1. Copper (II) Sulfate Reactions

The task to investigate the hydrogen-producing reaction of the copper (II) sulfate thermochemical cycle consists of three subtasks.

Task 1A. Polarization Studies

We measured the anodic and cathodic polarizations of the electrolysis of sulfurous acid (Reaction 1a) in a sulfuric acid electrolyte. Anodic and

cathodic polarizations were determined as a function of current density in electrolyte that is between 0 and 50 weight percent sulfuric acid. We prepared a Tafel plot and determined kinetic and diffusion-limited regions. We also determined the effect of temperature on anodic and cathodic polarizations for 33 weight percent sulfuric acid. Data were obtained for temperatures between 0° and 75°C.

Task 1B. Electrode Studies

We evaluated the catalytic behavior of selected electrode materials using shiny platinum as the basis for comparison. The electrode materials included platinum, platinum black, palladium (II) oxide, ruthenized titanium, and graphite. The catalytic behavior of each material was determined at 27°C in 33 weight percent sulfuric acid.

Task 1C. Copper (II) Sulfate Production

We conducted studies on the optimum method of producing copper (II) sulfate within the thermochemical cycle. The studies included an analysis of the direct electrolysis of sulfurous acid in the presence of copper (II) oxide (CuO) to determine the effect of the oxide on cell depolarization. We obtained data for three sulfuric acid concentrations and three temperatures.

Task 2. High Temperature Metal Sulfate Cycle

We conducted studies on the hydrogen-producing steps of metal sulfate cycles for use with very high temperature energy sources. These studies included the direct electrolysis of sulfurous acid in the presence of two metal oxides (other than CuO). The two metals (zinc and cadmium) chosen form complete metal sulfate thermochemical cycles which have significant process advantages over lower temperature cycles. Data were obtained for three sulfuric acid concentrations and three temperatures.

Additional Taskwork

We performed an additional series of experiments designed to alter the reaction mechanism by the addition of iodide ion to the anolyte. Anode performance in 33 weight percent sulfuric acid at 25°C was determined as a function of iodide ion concentration and electrode material.

TECHNICAL DISCUSSION

Equipment and Experimental Procedures

An H-cell constructed from 1-1/2-inch ID Pyrex-brand process pipe was used as a containment vessel for all experiments. The cell was coupled at the central bar of the "H" with aluminum flanges and neoprene O-rings. This configuration allowed easy installation of separator materials across the center junction to create isolated anode and cathode reservoirs, which were electrochemically accessible to each other only through the separator material. A Teflon coated magnetic bar at the bottom of each leg was used for stirring. For those experiments performed above and below ambient temperature, the cell was submerged to within 1 inch of the top in a well regulated water bath. Total capacity of the cell was 500 ml.

Sulfur dioxide was introduced into the anode chamber of the cell via a porous glass sparging tube. The top of this chamber was sealed with a neoprene stopper containing a small vent hole to assure an atmosphere of sulfur dioxide above the liquid level. No cap was used above the cathode chamber.

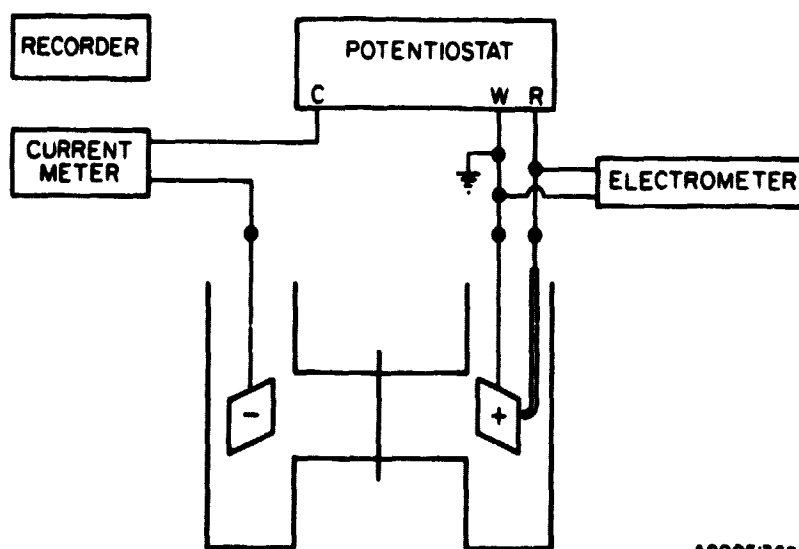
An AMEL Model 549 potentiostat was used to maintain a constant voltage between the working and reference electrodes during experiments. A Keithley 616 Digital Electrometer was used to monitor the voltage of the working electrode with respect to the reference. We used an Aardvark Model PEC-AM analog current meter to precisely monitor the flow of electric current and provide a current to voltage conversion for feed into a strip-chart recorder. Figure 1 is a schematic diagram of the H-cell and attendant instrumentation.

A fresh mercury/mercurous sulfate reference electrode was prepared 24 hours prior to each experimental run using sulfuric acid of the same concentration as in the day's experiments. However, all electrode potentials reported in this work (except where otherwise noted) are relative to an RHE. RHE potentials were calculated using measurements taken against the mercury/mercurous sulfate electrode and formulas provided by Bode.²

Table 1 contains a list of all materials and chemicals used on this project, their supplier, and the manufacturer-stated purity.

Table 1. MATERIALS AND SUPPLIERS

| <u>Material</u> | <u>Purity</u> | <u>Supplier</u> |
|---|---------------|-------------------|
| H ₂ SO ₄ | Reagent Grade | Fisher Scientific |
| CuSO ₄ ·5H ₂ O | Certified ACS | Fisher Scientific |
| ZnSO ₄ ·7H ₂ O | Certified ACS | Fisher Scientific |
| CdSO ₄ | Certified ACS | Fisher Scientific |
| CdO | Certified ACS | Fisher Scientific |
| KI | Certified ACS | Fisher Scientific |
| I ₂ | Certified ACS | Fisher Scientific |
| Hg | Purified | Fisher Scientific |
| PtCl ₄ ·2HCl·6H ₂ O | Reagent Grade | Fisher Scientific |
| Pt | 99.95% | Matthey Bishop |
| Hg ₂ SO ₄ | 99% | Alfa-Ventron |
| Pd | 99.9% | Alfa-Ventron |
| SO ₂ | 99.98% | Matheson |
| RVC | — | Fluorocarbon |
| Porous Graphite | — | POCO/Union 76 |



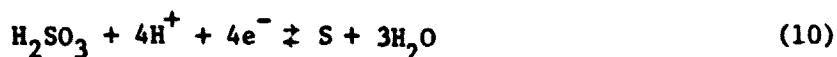
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Figure 1. SCHEMATIC DIAGRAM OF CELL AND INSTRUMENTATION

Preliminary Experiments

Separator Materials

Before electrochemical measurements of the anode reaction could be made, it was necessary to identify a separator material which would prevent or retard the diffusion of sulfur dioxide from the anode chamber to the cathode chamber. The chief problem associated with diffusion is the cathodic reduction of sulfur dioxide to form colloidal sulfur and hydrogen sulfide:



Because of its moderate solubility, hydrogen sulfide can return through the separator and poison the anode.

Three general classes of separators were evaluated: porous plastic, porous glass, and ion selective membranes. A 1-1/2-inch diameter separator was made from a representative material of each of the three classes and placed in the H-cell. A solution of distilled water saturated with sulfur dioxide was placed in one arm of the cell, while pure distilled water was placed in the other. After 1 hour, a sample was removed from the side initially containing pure distilled water and analyzed iodometrically for sulfur dioxide.

The three representative separators were (1) Daramic®, a porous plastic material manufactured by the W. R. Grace Co. for lead-acid batteries; (2) Nafion® 415, a positive ion selective membrane separator produced by DuPont for the chlor-alkali industry; and (3) Thirsty Vicor®, a porous glass manufactured by the Technical Products Division of Corning Glass. Table 2 lists the specifications for the three materials and presents the results of the diffusion experiments as moles of sulfur dioxide per cm² of separator per hour.

Table 2. SEPARATOR SPECIFICATIONS

| | Thickness, mil (mm) | Ionic* Resistance, ohm/cm ² | Average Pore Size, A | Diffusion Rate, mole/cm ² /hr |
|-------------------|------------------------|--|-------------------------|---|
| Daramic | 10 (0.25) | 0.5 | 500 | 1.3 X 10 ⁻² |
| Nafion 415 | 5 (0.13) | 3.3 | — | 7.9 X 10 ⁻⁴ |
| Thirsty Vicor 180 | 180 (4.6) | 3.5 | 80 | 3.3 X 10 ⁻⁶ |

* Soaked in 33 wt% H₂SO₄ prior to measurement of ionic resistance.

Thirsty Vicor proved to be the best separator. In the course of the program, cells with Thirsty Vicor separators were operated for several hours without the formation of colloidal sulfur in the cathode chamber. Although a separator 180 mils thick with an ionic resistance of 3.5 ohm/cm^2 would be far from satisfactory in a commercial process, it was satisfactory for an experimental cell.

Open Circuit Anode Potential

As discussed in the introduction, the equilibrium potentials for the anodic half-reaction calculated from thermodynamic values differ markedly from those measured in actual experiments. Furthermore, the anode potential measured on a smooth platinum surface depends more on the history of the electrode than on the concentration of the acid. Platinum electrodes which have been annealed (heated to redness) in air, or anodized in acid and placed opposite a reference electrode in a dilute sulfuric acid solution saturated with sulfur dioxide, exhibit a slowly changing potential. Figure 2 presents the results of such an experiment in three solutions ranging in concentration from 1 weight percent to 33 weight percent sulfuric acid. The potential between the mercury/mercurous sulfate reference and an annealed platinum electrode was monitored with a recording electrometer, and all measurements were converted to the reversible hydrogen scale. After 4 hours, the measurements made at three different acid concentrations converge (within the limits of experimental error) on a point 405 mV positive of reversible hydrogen. This suggests that the half-cell potential of the anodic reaction shows the same dependence upon acid concentration as the reversible hydrogen electrode.

Anode Passivation

One significant problem encountered in preliminary experiments concerned the passivation of smooth platinum anodes at moderate current densities. Clean platinum electrodes used as anodes for the oxidation of sulfur dioxide in dilute sulfuric acid exhibited excellent current densities for short periods of time. Over an extended period, however, the performance of these electrodes depreciated significantly. Figure 3 shows the results of experiments conducted on a 1-cm^2 smooth platinum electrode in 33 weight percent sulfuric acid saturated with sulfur dioxide. The 250 ml of solution contained

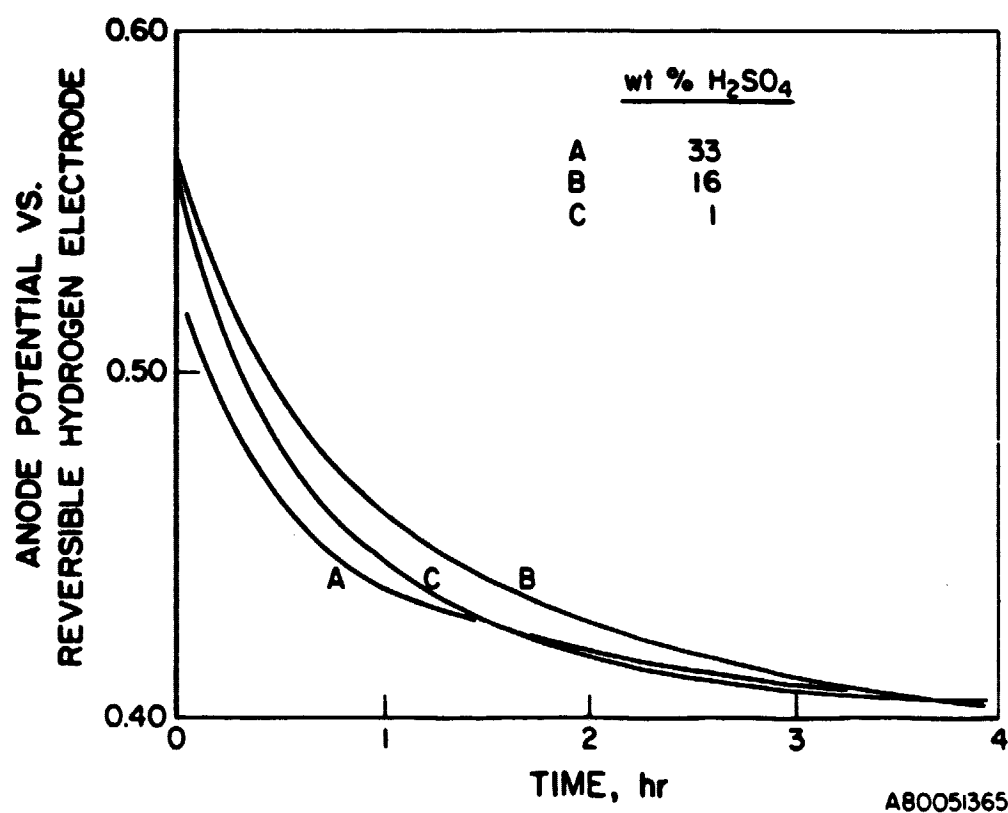


Figure 2. OPEN CIRCUIT ANODE POTENTIAL AS A FUNCTION OF TIME AND ACID CONCENTRATION (SO₂- Saturated H₂SO₄ Solution at 1 atm and 22°C)

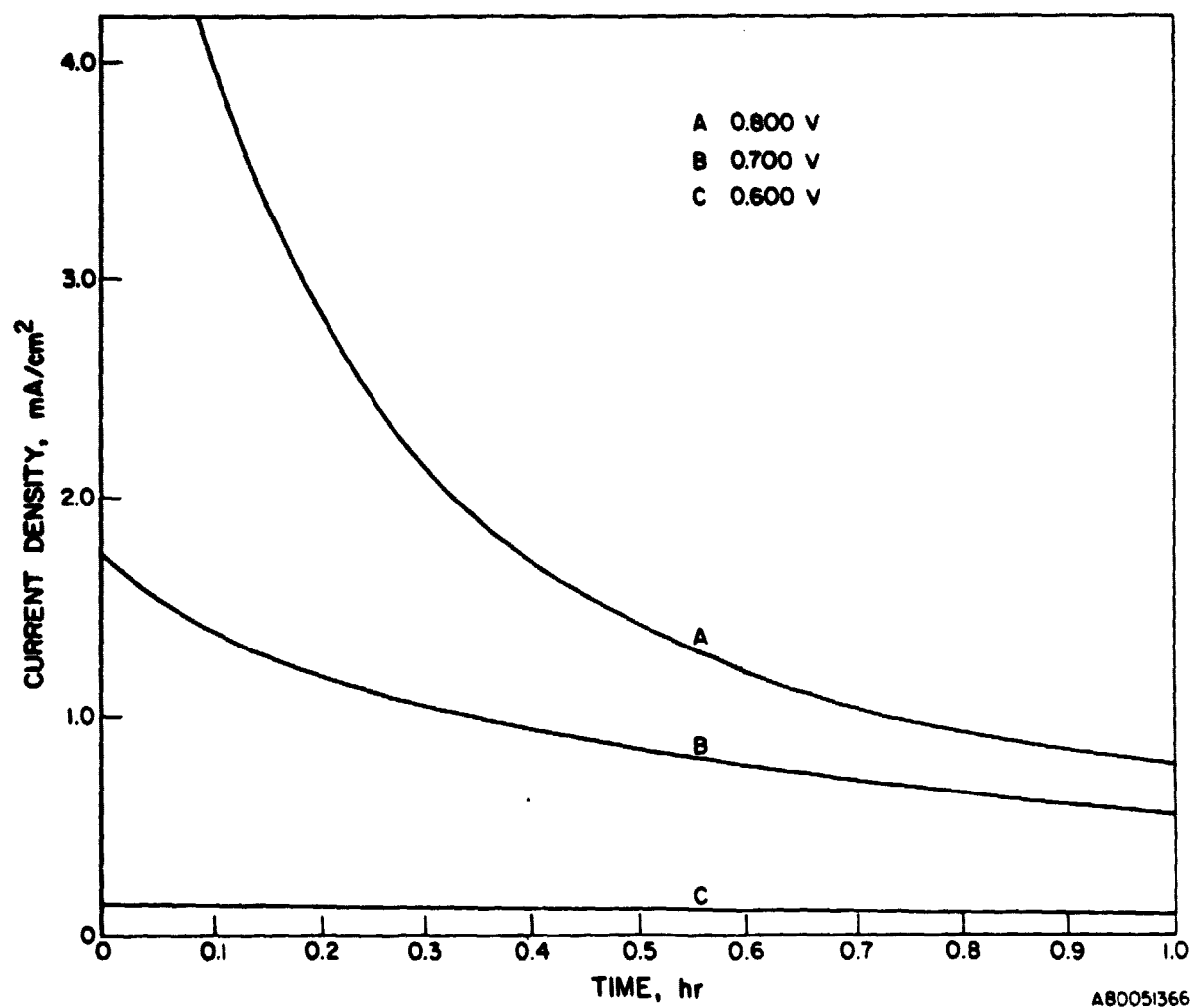


Figure 3. DECAY IN ANODE PERFORMANCE AS A FUNCTION OF ANODE POTENTIAL
(SO₂- Saturated 33 wt % H₂SO₄ at 1 atm and 22°C)

in the anode chamber was continuously stirred and sparged with sulfur dioxide at ~ 10 l/hr to assure the maintenance of saturation.

The platinum anode was first allowed to reach equilibrium with the solution and then potentiostated to 600, 700, or 800 mV positive of reversible hydrogen in separate experiments. Changes in current density were monitored for 1 hour with a recorder.

As Figure 3 shows, passivation of the electrode at 600 mV is slight compared to that at 800 mV. Also, the rate at which the electrode passivates under these conditions is considerably faster than can be attributed to either the consumption of reactants or the buildup of soluble reaction products. On the other hand, the rate of passivation is several orders of magnitude too slow to be consistent with the rapid depletion of an adsorbed monolayer.

Although this passivation phenomenon does not present a problem in the potential region of most interest (400 to 600 mV positive of reversible hydrogen), it does demonstrate the inadvisability of using linear-scan cyclic voltammetry to estimate equilibrium current densities. Determination of true equilibrium current densities at a stationary voltage by monitoring the long term passivation of the electrode, however, is impractical when a large number of measurements are to be made. As a result, a compromise procedure was developed that considers both the passivation phenomenon and the need to complete an experiment within a reasonable time frame.

Annealed or anodized electrodes were placed in solutions saturated with sulfur dioxide and allowed to come to equilibrium under a constant flow of sulfur dioxide gas. Using a potentiostat, the current density was measured at 50 mV intervals starting with the open circuit voltage. The potentiostat was indexed to the required potential and maintained at this potential for 5 minutes before reading the current density. Current densities measured in this manner are true equilibrium current densities within the region of interest (400 to 600 mV positive of reversible hydrogen).

Electrode Studies (Tasks 1A and 1B)Task 1A

The purpose of Task 1A was to determine the current-voltage characteristics of platinum electrodes for the oxidation of sulfur dioxide to sulfuric acid and the reduction of hydronium ion to hydrogen as a function of acid concentration and temperature.

Acid Concentration

Using the procedure and the H-cell described in the previous section, the relationship between the equilibrium current density and the overpotential for the cathode reaction was investigated in 1, 16, 33, and 50 weight percent H_2SO_4 . Table 3 lists these acid concentrations in alternate units of measurement. All cathode experiments were conducted in the absence of SO_2 .

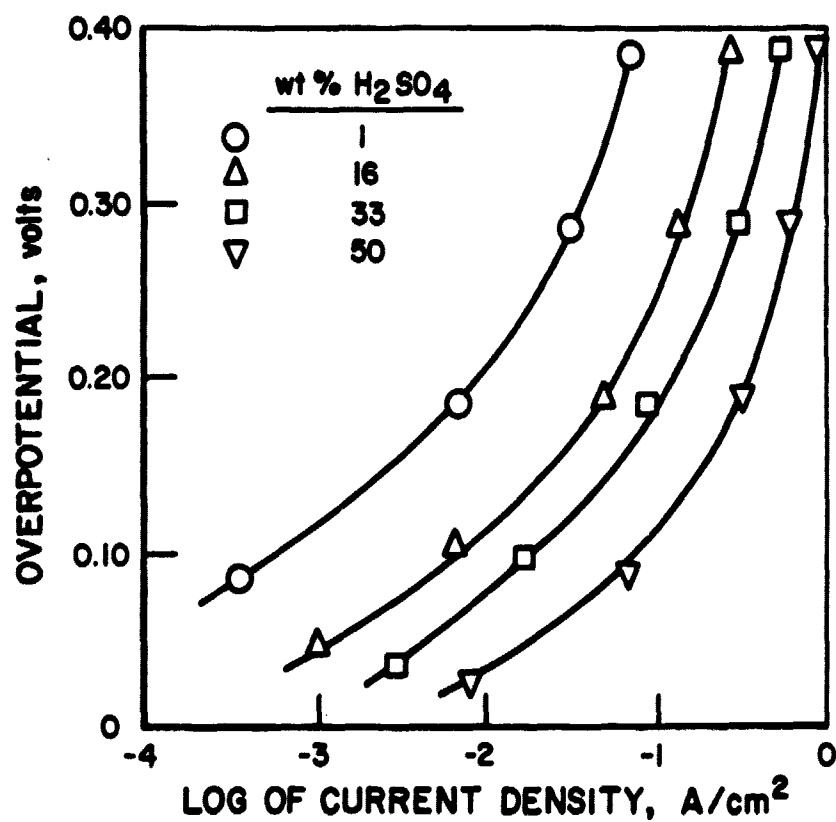
Table 3. ACID CONCENTRATIONS IN ALTERNATE UNITS

| <u>H_2SO_4, wt%</u> | <u>H_2SO_4, Vol%</u> | <u>Sp Gr at 25°C</u> | <u>Molality, m</u> | <u>Molarity, M</u> |
|--|---|--------------------------|--------------------|--------------------|
| 1 | 0.57 | 1.006 | 0.10 | 0.10 |
| 16 | 9.7 | 1.110 | 1.94 | 1.81 |
| 33 | 22.5 | 1.242 | 5.02 | 4.18 |
| 50 | 38 | 1.395 | 10.2 | 7.11 |

Figure 4 presents the results of these experiments. The current density at constant overpotential is more than an order of magnitude higher in 50 weight percent acid than in 1 weight percent acid on smooth platinum. Although the graph presents data in terms of overpotential, the half-cell reaction occurring at the cathode is also the half-cell reaction for the RHE. Thus, an overpotential of 100 mV coincides with minus 100 mV versus RHE regardless of the acid concentration.

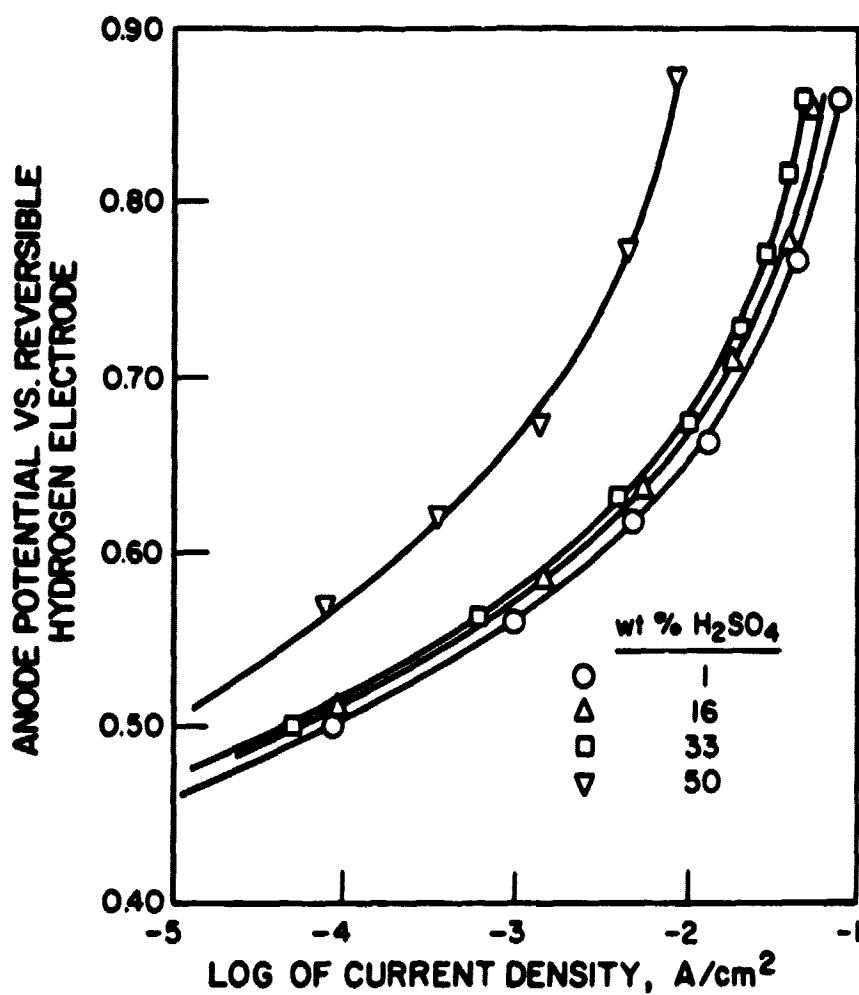
Similarly, the anodic polarization was determined as a function of current density in four acid concentrations using well stirred solutions saturated with sulfur dioxide at 1 atm and at 27°C. Figure 5 presents the results of these experiments.

The kinetics of the anode reaction are a relatively insensitive function of acid concentration between 1 and 33 weight percent H_2SO_4 , with slightly



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Figure 4. CURRENT DENSITY VERSUS OVERPOTENTIAL AS A FUNCTION OF ACID CONCENTRATION AT 27°C FOR THE REDUCTION OF HYDRONIUM ION ON SMOOTH PLATINUM



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Figure 5. CURRENT DENSITY VERSUS ANODE POTENTIAL AS A FUNCTION OF ACID CONCENTRATION AT 27°C FOR THE OXIDATION OF SULFUR DIOXIDE ON SMOOTH PLATINUM

better performances by the 1 weight percent acid. Differences that do exist may be more from physical differences in the solutions than an actual pH dependence. For example, 33 weight percent H_2SO_4 has a higher viscosity and ionic strength than 1 weight percent H_2SO_4 ; in addition, there is reason to believe that because of a lower activity coefficient for water in 33 weight percent H_2SO_4 , the solubility of SO_2 is also less.⁴ However the larger difference in performance between 33 and 50 weight percent acid cannot be explained solely on the basis of physical differences.

Our findings contradict results reported by others. B. D. Strück⁵ has observed a strong dependence between current density at constant overpotential and acid concentration in the range of 5 to 75 weight percent H_2SO_4 . A. J. Appleby¹, however, reports no dependence on acid concentration between 0.005 and 0.5 M (5 weight percent) H_2SO_4 in solutions of constant ionic strength, but significant differences at concentrations above 44 weight percent. This is consistent with our results within the limits of experimental error. The passivation phenomenon encountered in the preliminary experiments may figure heavily in attempts to account for these discrepancies. Strück⁵ performed his measurement using linear scan voltametry at sweep rates of 700 mV/s, and Appleby¹ used both potential scan and potentiostatic steady-state techniques to arrive at his conclusions.

At this point a conclusion can be made about the preferred acid concentration. The algebraic addition of the overpotentials reported in Figure 4 to the anode potentials versus RHE reported in Figure 5 yield IR-free cell voltages as a function of current density for each of the four acid concentrations. For example, the IR-free cell voltage on smooth platinum electrodes at a constant current density of 10 mA/cm² would be 850 mV in 1 weight percent acid, 785 mV in 16 weight percent acid, 675 mV in 33 weight percent acid, and 930 mV in 50 weight percent acid. Thus, on the basis of anode and cathode reaction kinetics using smooth platinum, 33 weight percent acid appears to be the preferred concentration.

Temperature

The relationship between current density and overpotential as a function of temperature was investigated using 33 weight percent sulfuric acid and smooth platinum electrodes. Experiments were conducted in a constant

temperature bath at 1°, 27°, 50°, and 75°C as measured in the anode chamber of the H-cell. The mercury/mercurous sulfate reference electrode was maintained at 27°C by a water jacket and fitted with a long Luggin capillary, over which the thermal gradient was distributed. The current-voltage characteristics of the cathode were determined in acid solutions free of SO₂, and anode measurements were determined in SO₂-saturated solutions using the potential-step technique previously described. Cathode kinetics as a function of temperature are shown in Figure 6 and anode kinetics in Figure 7. All data points have been removed for clarity.

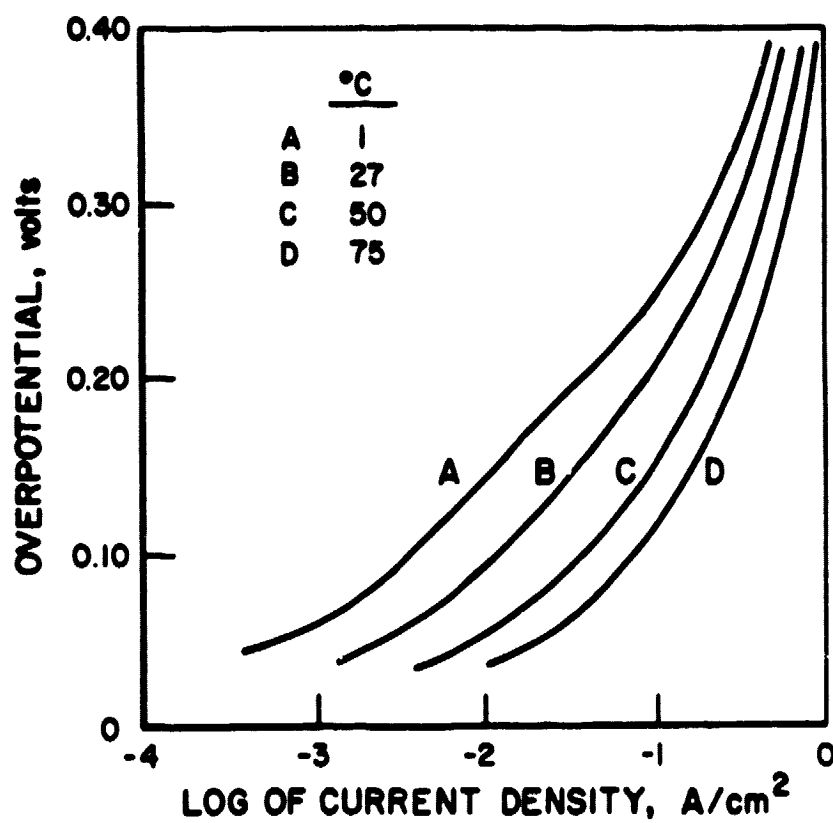
The rate of cathodic reduction of hydronium ion increased with increasing temperature at all overpotentials. However, the rate at which SO₂ is oxidized to sulfuric acid increased with increasing temperature only at low anode potentials (less than 600 mV RHE). As the anode potential increases, the temperature-current density relationship observed at 27°, 50°, and 75°C inverts. Because the solubility of SO₂ in aqueous solutions decreases with temperature (approaching zero at 100°C), the inversion of the current density-temperature relationship at high anodic potentials is probably from the concentration dependence of the SO₂ reaction. The decreased solubility of SO₂ at higher temperatures causes the onset of the mass transfer limited region at lower current densities. Therefore, if high SO₂ solubility can be achieved under pressure, it is reasonable to assume that a reduction in overpotential of about 80 mV can be affected on the cathode by operating at 75°C.

Task 1B

The purpose of Task 1B was to evaluate the catalytic behavior of a variety of materials used as anodes for the oxidation of sulfur dioxide. A 33 weight percent sulfuric acid solution saturated with sulfur dioxide was chosen as the preferred acid concentration and 27°C as the most convenient temperature. The 5 min/50 mV potential-step technique previously discussed was used in all Task 1B experiments. Results are summarized in Figure 8.

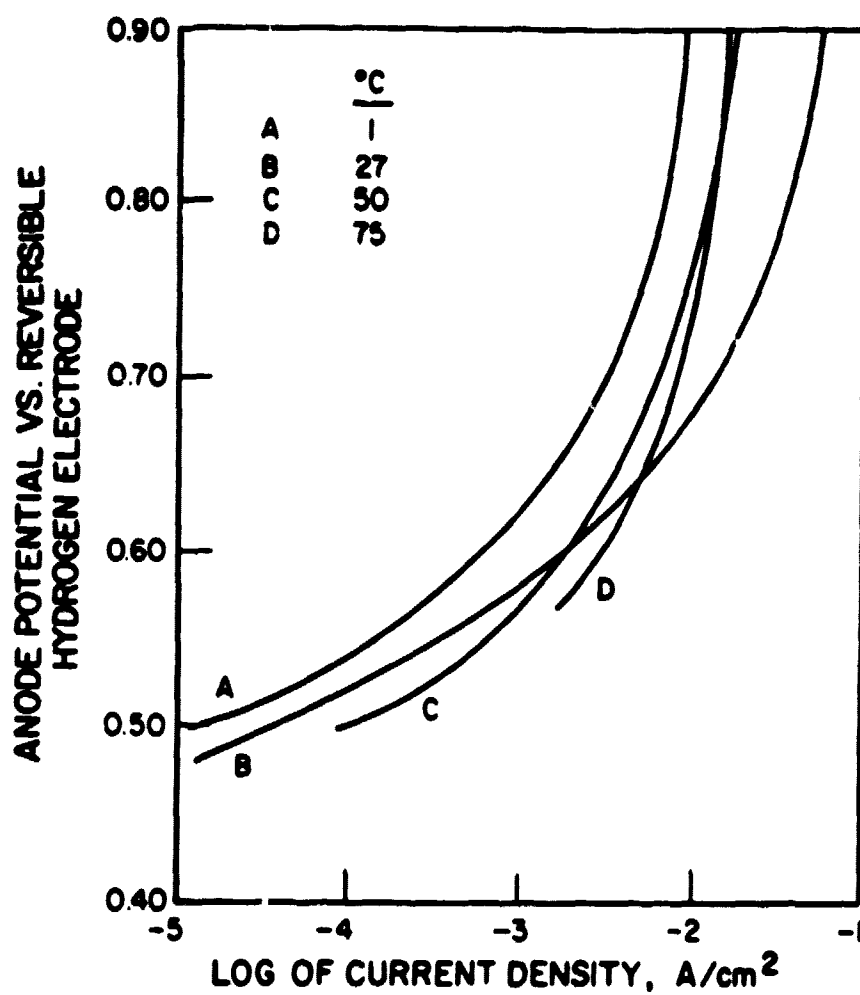
Ruthenized Titanium

An engineering sample of ruthenized titanium was obtained from a representative of the chlor-alkali industry. The sample was cut and mounted in paraffin wax with only 1 cm² of ruthenized surface exposed to the electrolyte. Equilibrium current densities as a function of anode potential are presented



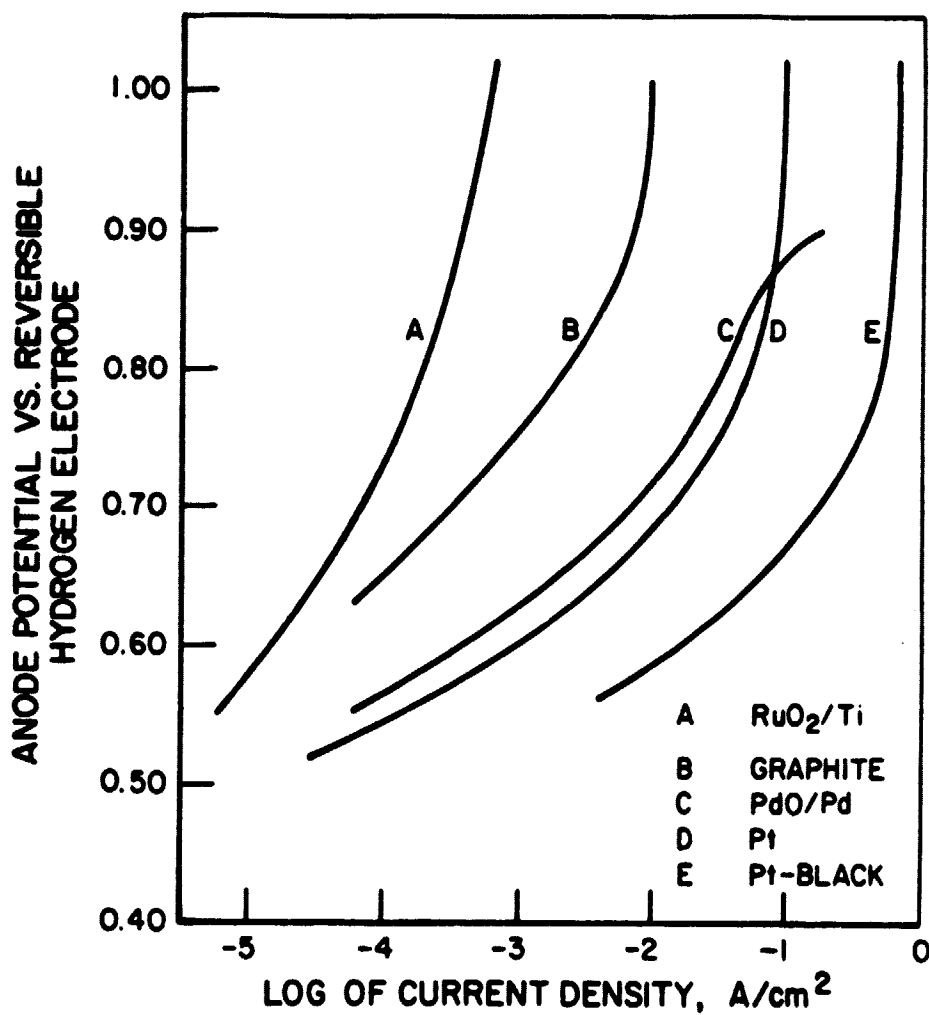
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Figure 6. OVERPOTENTIAL AS A FUNCTION OF TEMPERATURE FOR THE REDUCTION OF HYDRONIUM ION IN 33 wt% SULFURIC ACID



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Figure 7. OVERPOTENTIAL AS A FUNCTION OF TEMPERATURE FOR THE OXIDATION OF SULFUR DIOXIDE (33 wt% H₂SO₄ Saturated With SO₂ at 1 atm)



A79102280

Figure 8. TAFEL PLOTS FOR THE ELECTROCHEMICAL OXIDATION OF SO₂ ON VARIOUS CANDIDATE ANODE MATERIALS

in Curve A, Figure 8. The performance of this material was extremely poor, reaching only 10^{-4} A/cm² at an anode potential of 800 mV positive of RHE.

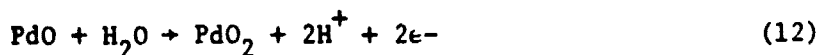
Porous Graphite

Porous high surface area graphite was obtained from POCO, a division of Union-76. The material was cut to 1 cm² and a titanium wire was attached to the back side using silver epoxy. The back side, including epoxy, was then covered with hot paraffin wax. As shown by Curve B in Figure 8, the graphite electrode performed somewhat better than the ruthenized titanium, but was still two orders of magnitude below the project goal of 200 mA/cm².

Palladium Oxide

Palladium oxide was also evaluated as a candidate anode material. Palladium oxides can be obtained in three common forms: PdO, PdO·xH₂O, and PdO₂·xH₂O. Of these three, only the anhydrous monoxide is insoluble in acid under our conditions. Palladium oxide electrodes were fabricated by heating a palladium foil electrode in air. The temperature range over which this can be accomplished is narrow, because decomposition of PdO occurs at temperatures above 750°C. Fortunately, PdO is a dark blue color and its growth on the surface of a metal foil electrode can be easily observed. A uniform layer of the blue oxide could be built up by placing a palladium foil electrode above the flame of a gas burner. Curve C of Figure 8 shows that the PdO coated electrode performed nearly as well as a smooth platinum electrode at low anodic potentials under the same conditions.

The PdO layer was significantly corroded, however, at potentials above 850 mV RHE, presumably from the oxidation of palladium (II) to palladium (IV):



Corrosion was accompanied by the disappearance of the oxide color and the appearance of a yellow tint within the acid solution. Because anode potentials in excess of 600 mV RHE are not expected in a practical device, it is conceivable that performances equal to that of smooth platinum could be achieved with optimization of the PdO layer.

Platinum Black

Platinum black electrodes, also known as "platinized platinum" were fabricated from platinum foil and chloroplatinic acid. A 1-cm² platinum

foil electrode was surface roughened, cleaned, and placed in a 0.3% chloroplatinic acid solution containing a trace of lead acetate. A counter electrode of smooth platinum was used. A 10 Hz pulsed dc potential was applied to the electrode and adjusted to a peak current density of 40 mA/cm^2 . Electrodeposition of platinum on the platinum foil was continued until what was initially a grey surface deposit had turned black. The platinum black electrode was then washed with and soaked in distilled water for 24 hours prior to loading in the experimental cell.

Curve E is a graph of the results of the platinum black experiments. The platinum black electrode succeeded in breaking the 200 mA/cm^2 barrier at slightly less than 700 mV RHE.

Discussion

At the conclusion of Task 1, a serious discrepancy existed between our results and the results of others in the field. B. D. Strück⁵ claims to have investigated 50 non-noble materials as possible electrocatalysts for the SO_2 oxidation reaction and found none better than platinum. This conclusion is compatible with our results in light of the limited number of materials we have tested. However, Westinghouse⁴ claims that two proprietary materials show electrocatalytic performance superior to platinum. Material WAE 2 is reported to be 4 times better than platinum, and WAE 3 is 30 times better. The major discrepancies arise not with claims for the proprietary electrodes but with the published results for platinum. Parker reports a Tafel slope of 67 mV/decade, exchange current densities of $1.9 \times 10^{-7} \text{ mA/cm}^2$, and limiting current densities of 1.2 mA/cm^2 at anode potentials +770 mV RHE for the oxidation of SO_2 on platinum in 50 weight percent acid. We observed Tafel slopes of 55 mV/decade, exchange current densities of $3 \times 10^{-7} \text{ mA/cm}^2$, and limiting current density of 11 mA/cm^2 at 940 mV RHE under the same conditions. In addition, we have observed limiting current densities of 100 mA/cm^2 in 33 weight percent acid on smooth platinum and 675 mA/cm^2 on platinum black electrodes.

These discrepancies can be resolved if we accept several as yet unproven assumptions concerning the origin of the passivating layer described in the preliminary experiments. Figure 9 is a current-voltage plot similar to Figure 5 but extended to potentials 2.0 V positive of RHE. Data were obtained using the 50 mV/5 min potential-step technique previously discussed.

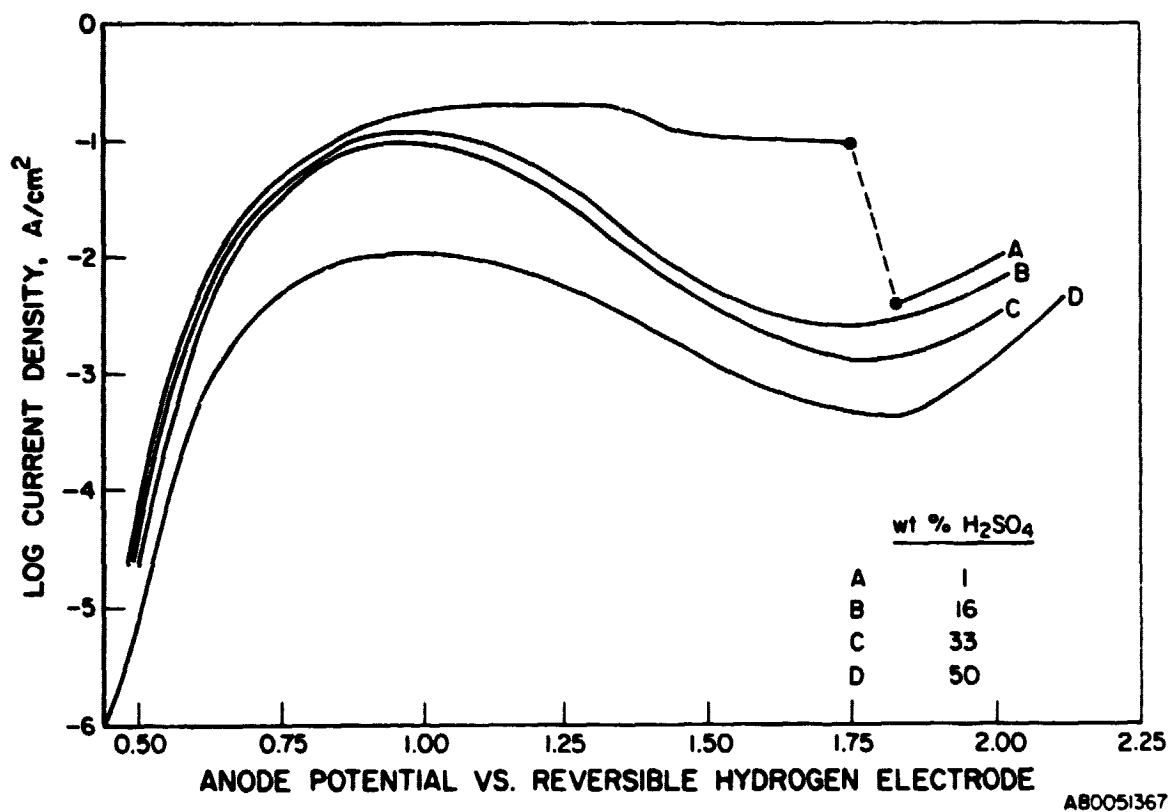


Figure 9. ELECTRODE PERFORMANCE AT HIGH ANODIC POTENTIALS
(SO₂- Saturated H₂SO₄ Solution at 1 atm and 22°C)

However, because a full 2.7 hours were required to reach the final voltage, Figure 9 also represents a linear scan potentiograph with a scan rate of 10 mV/min. Peak current densities are reached at about 950 mV RHE, but unlike limiting current densities resulting from mass transfer limitations, the performance here decays at higher potentials. Because of the large volume of reactants available and the slow scan rate, this decrease in performance can only be attributed to a passivation phenomenon. It should also be noted that in the potential region from 1.5 to 1.75 V where strong oxygen evolution is observed in dilute SO_2 -free sulfuric acid, the current density in the presence of SO_2 continues to decrease. This indicates that the phenomenon inhibiting the SO_2 oxidation reaction is also blocking the oxygen evolution reaction. The absence of oxygen evolution in an operating cell containing SO_2 in the anolyte was verified visually.

Unusual performance is also exhibited by 1 weight percent sulfuric acid solutions saturated with SO_2 . A metastable condition appears to develop on smooth platinum in 1 weight percent acid in potential regions where the same electrode has already begun to passivate in solutions of higher concentration. This metastable condition fails suddenly, and yields a curve paralleling that observed in acid solutions of higher concentration. Although the phenomenon of sudden passivation could be reproduced in 1 weight percent acid, the potential at which the onset of failure occurred was between 1.25 and 1.8 V and not reproducible.

Data presented in Figure 9 indicate an inverse relationship between the passivation phenomenon and acid concentration. Furthermore, the onset of the passivation phenomenon roughly corresponds with the point where adsorbed oxygen first appears in cyclic voltammograms of smooth platinum in SO_2 -free sulfuric acid solutions. Coupled with the suppression of the oxygen evolution reaction at higher anode potentials, this suggests that surface oxides, which are known to catalyze this latter reaction, are intimately involved in the passivation phenomenon.

If this is true, then the practice followed by Westinghouse⁴ and others of anodizing test electrodes prior to use could have an adverse effect upon their performance and lead to the report of low current densities. This is supported by the fact that the minimum in the 50 weight percent current

density curve which we observe at 1.8 volts is below the limiting current density reported by Westinghouse, although our peak performance is an order of magnitude better. Westinghouse also reports open circuit anode potentials at 480 mV RHE after 4 hours in 50 weight percent sulfuric acid saturated with SO_2 . We observe, however, potentials at 405 mV after 4 hours with annealed electrodes, suggesting that anodized electrodes start out in a partially passivated state.

Because we have not observed passivation at anode potentials below 600 mV-RHE, and a practical cell must for purposes of efficiency operate below this potential, we feel our data are more representative of the performance that can be expected from platinum electrodes in this system.

Metal Sulfate Production (Tasks 1C, 2A, and 2B)

The purpose of Tasks 1C, 2A, and 2B was to determine the method for the production of metal sulfate most compatible with the electrochemical step. There are three possible methods for producing metal sulfate from metal oxide and sulfuric acid which do not require the evaporation of excess solvent:

1. The reaction of excess acid with metal oxide in an external vessel to form a hot, saturated solution of metal sulfate. This is followed by the crystallization of the metal sulfate by cooling the solution.
2. The reaction of sulfuric acid with an excess of metal oxide to produce a neutral saturated solution of metal sulfate. After filtration to remove unreacted metal oxide, the metal sulfate is precipitated using the common ion effect through the addition of more sulfuric acid.
3. The addition of metal oxide directly to the anode chamber neutralizing some of the acid followed by operation of the cell to regenerate the acid and force the metal sulfate to precipitate as the result of the common ion effect.

All three methods suffer the same handicap: Substantial quantities of metal sulfate must either be returned to or maintained in the anolyte during the electrochemical reaction. Electrochemical studies were undertaken to determine the performance of smooth platinum electrodes in the presence of metal sulfate. The ability of smooth platinum to catalyze the oxidation of SO_2 to H_2SO_4 in the presence of metal sulfate was evaluated at 22°C in acid concentrations of 1, 16, and 33 weight percent sulfuric acid, and in 33 weight

percent acid at temperatures of 22°, 50°, and 70°C. A circular, smooth platinum electrode of 0.85 cm² area was mounted in plastic so that only the front surface was exposed to the electrolyte. The electrode was cleaned by anodization in sulfuric acid solutions for 10 minutes at 100 mA/cm² current density. The test electrode was then maintained at open circuit while the anolyte was saturated with SO₂. The metal sulfate was then added and dissolved (with stirring) under a continuous flow of SO₂. The 50 mV/5 min potential-step technique previously described was used to measure current density as a function of anode potential.

For convenience, anodization was chosen as the preferred method of cleaning these electrodes before the full importance of the passivation phenomenon was realized. When it became apparent that a significant difference existed between the performance of anodized electrodes and annealed electrodes, a second series of experiments was conducted using anodized electrodes, in pure dilute acid similar to the experiments conducted in Task 1A with annealed electrodes. The results of Tasks 1C, 2A, and 2B are summarized in five tables. The results of the dilute acid experiments without metal sulfate on anodized electrodes are included for convenient reference.

Task 1C

Task 1C used copper sulfate as the metal sulfate added. Enough copper sulfate pentahydrate was added to the anode chamber to produce a 0.25 M solution. This concentration produces a saturated solution at 22°C in 33 weight percent acid. For consistency the same concentration was used in all other tests. However, 0.25 M copper sulfate is an unsaturated solution in 1 and 16 weight percent acid at 22°C and 33 weight percent at 50° and 70°C

Task 2A

Task 2A experiments were identical to those in Task 1C, except that 0.25 M zinc sulfate was used as the metal sulfate.

Zinc sulfate has an advantage over copper sulfate because of its retrograde solubility approaching 0 at 250°C in pressurized water. Furthermore, the species precipitating from pressurized water is a monohydrate rather than the heptahydrate obtained at ambient temperatures. Thus, zinc sulfate may provide a unique and possibly energy efficient means of both precipitating and drying the metal sulfate product in one step.

Task 2B

The 1 weight percent sulfuric acid experiments in Task 2B were performed in the same way as those in Tasks 1C and 2A but using cadmium sulfate. In the 16 and 33 weight percent experiments, however, cadmium oxide was added to the acid solution rather than cadmium sulfate. The cadmium oxide reacted with the acid to produce a 0.25 M cadmium sulfate solution. This change in procedure provided a series of experiments in which a constant sulfate concentration was maintained between the pure dilute acid and the metal sulfate runs.

Discussion

Tables 4 through 8 summarize the results of the Task 1C, 2A, and 2B experiments. Anodic potential was measured versus a mercury/mercurous sulfate reference and corrected to RHE. Anodic current is the actual current observed on a 0.85 cm^2 electrode. Data are grouped on the basis of acid concentration and temperature; with the results of identical experiments conducted without acid; with CuSO_4 ; ZnSO_4 ; and with CdSO_4 or CdO appearing together.

Although the performance characteristics of the smooth platinum electrodes used for the oxidation of SO_2 in the presence of metal sulfates can be deduced from Tables 4 through 8 the relationships cannot be explained. The presence of copper sulfate in the SO_2 -saturated sulfuric acid solutions increased the overpotential for SO_2 oxidation above that observed in metal-free solutions. This increase ranged from about 50 mV in 1 weight percent acid to over 250 mV in 33 weight percent acid at high temperatures. Zinc sulfate caused an even greater increase in overpotential and the addition of cadmium sulfate all but shut down the reaction.

A small effect was also noted on the equilibrium open circuit anode potential. The addition of copper sulfate raised the open circuit anode potential, and zinc sulfate lowered them. Cadmium sulfate raised the observed potentials in 1 and 16 weight percent acid but lowered them in 33 weight percent acid.

No correlation could be found between changes in open circuit anode potential and electrode performance. Different concentrations of sulfate ions, hydrogen sulfate ions, hydronium ions, or water also failed to explain

Table 4. ANODIC CURRENT ON PLATINUM ELECTRODES FOR THE OXIDATION OF SO_2 IN 1 WT% ACID AT 22°C

| Anode Potential vs RHE | Anodic Current, mA | | | |
|------------------------------|--------------------|-------------------------|-------------------------|-------------------------|
| | Acid Only | With CuSO_4 | With ZnSO_4 | With CdSO_4 |
| 0.525 | 0.74 | — | — | — |
| 0.575 | 2.2 | 0.66 | 1.1 | 0.02 |
| 0.625 | 5.1 | 2.8 | 2.3 | 0.027 |
| 0.675 | 8.2 | 6.4 | 6.0 | 0.052 |
| 0.725 | 16 | 9.2 | 8.1 | 0.075 |
| 0.775 | 24 | 19 | 12 | 0.095 |
| 0.825 | 34 | 27 | 16 | 0.16 |
| 0.875 | 45 | 36 | 22 | 0.29 |
| 0.925 | 56 | 46 | 30 | 0.55 |
| 0.975 | 68 | 56 | 35 | 1.1 |
| 1.025 | 80 | 67 | 41 | 1.9 |
| 1.075 | 93 | 78 | 47 | 2.9 |
| 1.125 | 108 | 88 | 52 | 4.0 |
| Open Circuit Anode Potential | | | | |
| | 0.440 | 0.482 | 0.431 | 0.460 |

Table 5. ANODIC CURRENT ON PLATINUM ELECTRODES FOR THE OXIDATION OF SO_2 IN 16 WT% ACID AT 22°C

| Anode Potential vs RHE | Anodic Current, mA | | | |
|------------------------------|--------------------|-------------------------|-------------------------|----------------------|
| | Acid Only | With CuSO_4 | With ZnSO_4 | With CdO |
| 0.540 | 0.020 | — | 0.009 | — |
| 0.590 | 0.11 | — | 0.052 | 0.1 |
| 0.640 | 0.66 | 0.73 | 0.36 | 0.48 |
| 0.690 | 3.1 | 1.4 | 0.9 | 1.2 |
| 0.740 | 7.7 | 1.9 | 2.0 | 2.4 |
| 0.790 | 15 | 3.4 | 3.4 | 4.1 |
| 0.840 | 25 | 6.1 | 5.0 | 6.0 |
| 0.890 | 36 | 11.5 | 6.5 | 8.4 |
| 0.940 | 44 | 19.0 | 9.0 | 12 |
| 0.990 | 49 | 29 | 12 | 15 |
| 1.040 | 50 | 36 | 16 | 17 |
| Open Circuit Anode Potential | | | | |
| | 0.460 | 0.484 | 0.454 | 0.470 |

Table 6. ANODIC CURRENT ON PLATINUM ELECTRODES FOR THE OXIDATION OF SO_2 IN 33 WT% ACID AT 22°C

| Anode Potential vs RHE | Anodic Current, mA | | | |
|------------------------------|--------------------|-------------------------|-------------------------|----------------------|
| | Acid Only | With CuSO_4 | With ZnSO_4 | With CdO |
| + 0.500 | 0.005 | — | — | — |
| 0.550 | 0.015 | — | — | — |
| 0.600 | 0.095 | 0.10 | 0.080 | 0.12 |
| 0.650 | 0.52 | 0.43 | 0.23 | 0.14 |
| 0.700 | 1.7 | 1.6 | 0.50 | 0.22 |
| 0.750 | 4.0 | 3.8 | 0.95 | 0.28 |
| 0.800 | 7.5 | 4.5 | 1.4 | 0.35 |
| 0.850 | 12 | 6.3 | 1.9 | 0.41 |
| 0.900 | 15 | 8.0 | 2.3 | 0.49 |
| 0.950 | 17 | 10 | 2.7 | 0.59 |
| 1.000 | 18 | 12 | 3.2 | 0.73 |
| Open Circuit Anode Potential | | | | |
| | 0.480 | 0.507 | 0.472 | 0.432 |

Table 7. ANODIC CURRENT ON PLATINUM ELECTRODES FOR THE OXIDATION OF SO₂ IN 33 WT% ACID AT 50°C

| Anode Potential vs RHE | Anodic Current, mA | | | |
|------------------------------|--------------------|---------------------------|---------------------------|-------------|
| | Acid Only | With CuSO ₄ | With ZnSO ₄ | With CdO |
| +0.500 | — | — | — | 0.030 |
| 0.550 | 0.07 | 0.03 | 0.01 | 0.055 |
| 0.600 | 0.62 | 0.06 | 0.12 | 0.12 |
| 0.650 | 2.4 | 0.14 | 0.28 | 0.23 |
| 0.700 | 6.2 | 0.21 | 0.49 | 0.31 |
| 0.750 | 10 | 0.33 | 0.73 | 0.33 |
| 0.800 | 13 | 0.46 | 0.98 | 0.35 |
| 0.850 | 12 | 0.61 | 1.2 | 0.38 |
| 0.900 | 10 | 0.80 | 1.6 | 0.49 |
| 0.950 | 8.8 | 1.1 | 2.0 | 0.78 |
| 1.000 | 9.3 | 1.3 | 2.5 | 2.2 |
| Open Circuit Anode Potential | | | | |
| | 0.503 | 0.507 | 0.492 | 0.436 |

Table 8. ANODIC CURRENT ON PLATINUM ELECTRODES FOR THE OXIDATION OF SO_2 IN 33 WT% ACID AT 70°C

| Anode Potential vs RHE | Anodic Current, mA | | | |
|------------------------------|--------------------|-------------------------|-------------------------|----------------------|
| | Acid Only | With CuSO_4 | With ZnSO_4 | With CdO |
| +0.500 | — | — | 0.015 | 0.06 |
| 0.550 | 0.044 | 0.050 | 0.040 | 0.06 |
| 0.600 | 0.15 | 0.10 | 0.10 | 0.07 |
| 0.650 | 0.36 | 0.28 | 0.22 | 0.12 |
| 0.700 | 0.69 | 0.30 | 0.33 | 0.14 |
| 0.750 | 1.1 | 0.42 | 0.45 | 0.22 |
| 0.800 | 1.4 | 0.59 | 0.57 | 0.28 |
| 0.850 | 1.8 | 0.74 | 0.73 | 0.35 |
| 0.900 | 2.2 | 0.80 | 1.1 | 0.41 |
| 0.950 | 2.9 | 1.1 | 1.4 | 0.49 |
| 1.000 | 3.9 | 1.3 | 1.7 | 0.59 |
| Open Circuit Anode Potential | | | | |
| | +0.500 | +0.512 | +0.492 | +0.410 |

changes in the magnitude and direction of the open circuit anode potential or the electrode performance. Similarly, the differences in performance of the platinum electrode could not be related to any physical or electrochemical property of the respective metal sulfate.

One conclusion can be reached, however: The presence of metal sulfate in the electrolyte adversely affects the performance of smooth platinum electrodes.

Homogeneous Catalysis Using Iodine

Midway through the program, information provided by B. D. Strück⁵ indicated that small amounts of hydrogen iodide can be used as a homogeneous catalyst for the electrochemical oxidation of sulfur dioxide. A series of experiments were performed to assess this effect.

The theory behind this approach is that the electrochemistry occurring on the anode will be the oxidation of iodide to iodine (more correctly tri-iodide) rather than the oxidation of sulfur dioxide to sulfuric acid.



The standard reduction potential for this reaction is 0.545 V. However, iodine reacts with sulfur dioxide to produce sulfuric acid and regenerate iodide ion via the well-known Bunsen reaction:



As a consequence, the build up of iodine in solution is prevented so that the iodide concentration is always much greater than the iodine concentration. The relative proportions of iodide and iodine affect the half-cell potential such that if the I^-/I_2 ratio is 1000, the anodic half cell potential is reduced to 0.368 V. In fact, actual open circuit anode potentials measured in 30 weight percent sulfuric acid saturated with sulfur dioxide at 25°C with 0.05 M potassium iodide are on the order of 0.240 V versus RHE. This open circuit potential is considerably better than the 0.405 V RHE observed in the absence of iodide ion and is close to the thermodynamic value of 0.170 V calculated for the SO_2 reaction.

Experimental Results

Two series of experiments were conducted using potassium iodide as an additive to the anode chamber. In the first series, smooth platinum electrodes

were placed in 33 weight percent sulfuric acid solutions saturated with SO_2 at 25°C and containing 0.01, 0.02, and 0.05 M potassium iodide, respectively. The current-voltage characteristics of the platinum anodes were determined using the potential-step techniques.

Two results were immediately obvious: (1) The open circuit anode potential was now about 240 mV versus RHE instead of 405 mV RHE, and (2) stable open circuit anode potentials were reached within minutes instead of hours. Figure 10 presents the results of this series of experiments as a plot of anode potential against current density. These coordinates were chosen in place of the standard Tafel plot to better illustrate the direct relationship between electrode performance and iodide concentration.

The second series of experiments evaluated the performance of six candidate electrodes in an SO_2 -saturated 33 weight percent sulfuric acid solution containing 0.05 M KI. Figure 11 presents the results of these experiments as Tafel plots.

In order to minimize edge effects, electrodes of 5 cm² frontal area were constructed. All electrodes were then mounted in wax so that only the front face was accessible to the electrolyte. The following candidate electrode materials were evaluated at 25°C:

1. RVC-105 (Reticulated Vitreous Carbon). RVC-105 is a porous glassy carbon which has a coarse pore structure with a large void space. Prior to use this electrode was anodized at 100 mA/cm² for 10 minutes in 33 weight percent sulfuric acid to increase its effective surface area by etching the glassy carbon fibers.
2. RVC-1005. This glassy carbon material has a medium-coarse pore structure with about 10 times the actual surface area per unit frontal area as RVC-105. This electrode was also etched prior to use.
3. POCO Graphite. This electrode was fabricated from an engineering sample of porous graphite provided by POCO, a division of Union-76. No information concerning the actual surface area was available, but examination with an optical microscope indicated a very fine pore structure. This electrode was not etched prior to use.
4. Smooth Platinum. The electrode was anodized prior to use.
5. Platinized RVC-1005. This electrode was fabricated by electroplating platinum onto Electrode No. 2. The approximate

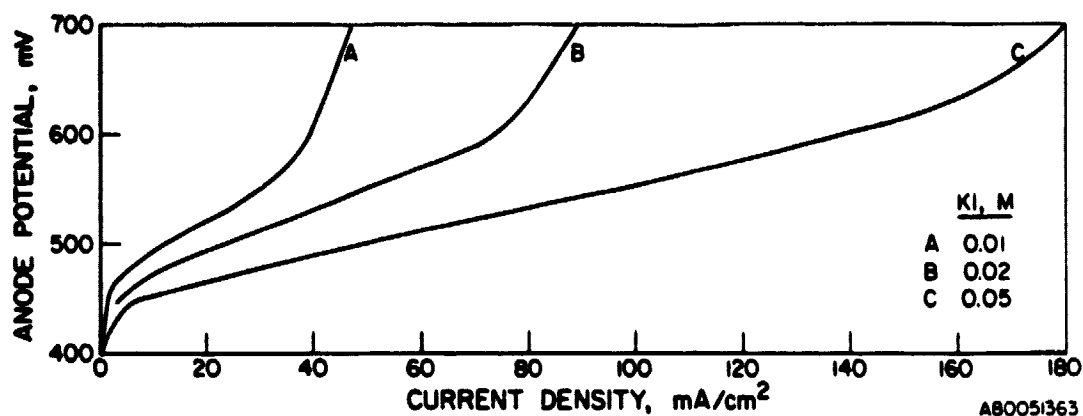


Figure 10. EFFECT OF IODIDE CONCENTRATION ON ELECTRODE KINETICS

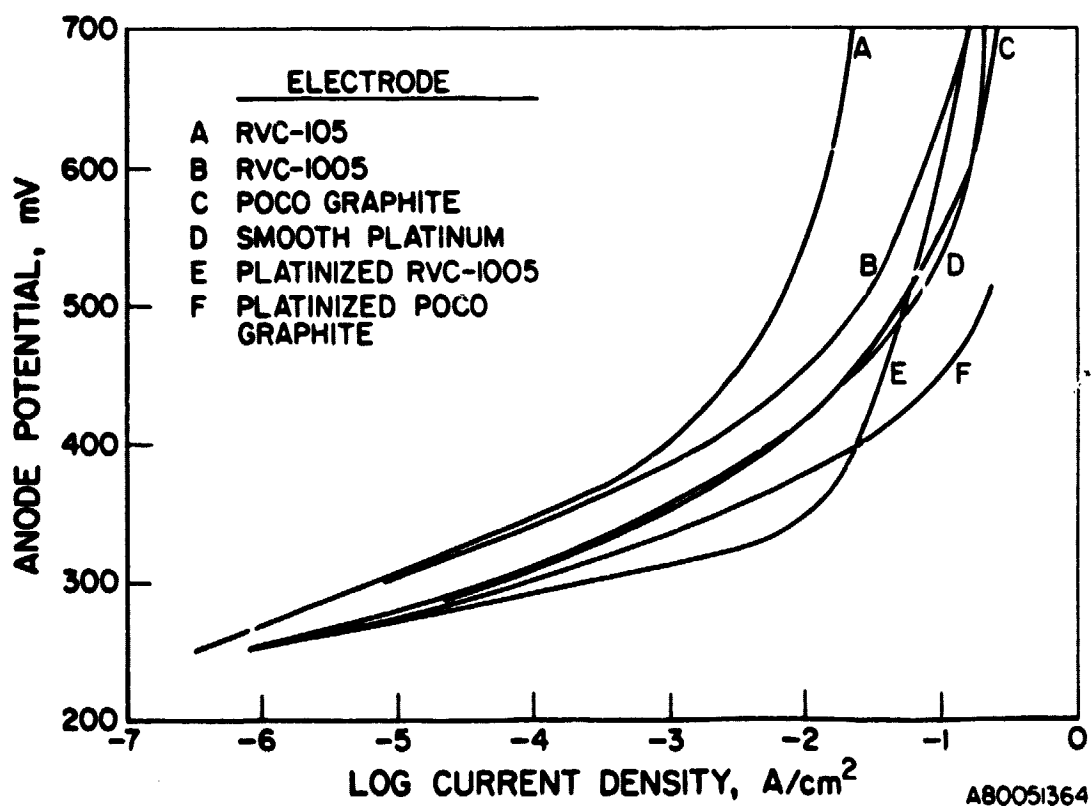


Figure 11. PERFORMANCE OF VARIOUS CANDIDATE ELECTRODES IN THE PRESENCE OF 0.05M KI

loading of platinum was 2 mg/cm^2 of frontal area. Sectioning of the electrode after use and microscopic examination of a cleaned edge indicated that most of the platinum was deposited on the top few glassy fibers.

6. Platinized POCO Graphite. This electrode was prepared by electroplating platinum onto Electrode No. 3. The approximate loading of platinum was 1 mg/cm^2 of frontal area.

Discussion

It is apparent from Figure 10 that the current density on smooth platinum is related in an almost linear fashion to the concentration of iodide ion at any given potential. Figure 11 indicates there is at least a qualitative relationship between performance and surface area of the three carbon electrodes tested. Figure 11 also suggests that platinizing enhances the performance of carbon based electrodes.

However, conclusions concerning the limiting current density of a particular electrode geometry should not be drawn from Figure 11. Differences in the accessibility of the electrolyte to the interior of the porous electrodes probably accounts for the observed limiting currents rather than actual catalytic properties. For example, optical examinations indicate that nearly all of the platinum electrode deposited on RVC-1005 was placed on a relatively few carbon fibers. At low current density almost the entire reaction is carried by these platinized fibers. But at higher current densities, these fibers reach their mass transfer limit first, and the performance curve of the platinized electrode (No. 5) approaches that of the platinum free electrode (No. 2). Examination of the platinized POCO graphite indicates that platinum was also deposited only on the front of the porous surface. However, because of its extremely tight pore structure, the internal surfaces probably contributed very little to the electrochemistry of either electrode No. 3 or No. 6. Thus, a properly platinized RVC-1005 electrode which is uniform throughout could possibly out perform even the POCO graphite at high current densities.

Although time did not permit the systematic investigation of electrode kinetics in the presence of both potassium iodide and metal sulfate, qualitative experiments indicated that KI is an effective homogeneous catalyst in the presence of either zinc sulfate or cadmium sulfate. Potassium iodide is

incompatible with copper sulfate in the presence of sulfur dioxide, however, and a reaction occurs which results in a white precipitate of copper (I) salts.

One factor, as yet untested, which can be expected to improve anode performance in the presence of iodine is an increase in temperature. No problems are envisioned with respect to iodine volatility at high temperatures, because in the presence of excess SO_2 virtually all of the catalyst exists in solution as iodide ion. However, it is expected that a substantial increase in SO_2 pressure will be required to maintain this excess of SO_2 at high temperatures and high current densities.

Because it is a fully reduced species, iodide ion cannot undergo reaction at the cathode and will not present a problem should small amounts of iodide reach the cathode chamber. Iodine, on the other hand, can be reduced at the cathode. In the present system, however, substantial iodine concentrations exist only in the immediate vicinity of the anode.

The best performance observed to date on an unoptimized electrode with potassium iodide as a catalytic agent indicated a current density of 100 mA/cm^2 at a projected cell voltage of 600 mV. There is every reason to believe that with proper electrode development and the application of higher temperatures and pressures, the project goals of 200 mA/cm^2 at a cell voltage of 500 mV can be achieved.

CONCLUSIONS AND RECOMMENDATIONS

The purpose of this program was to assess the electrochemical oxidation of sulfur dioxide in relatively dilute (less than 50 weight percent) sulfuric acid and to determine the preferred operating conditions (acid concentration, temperature, electrode materials) for such a cell to be mated with a metal oxide-metal sulfate water-splitting cycle. Based on extensive thermodynamic evaluations of hybrid water-splitting cycles, we estimate that total cell voltages of 0.5 V or less are desired to compete with electrolytic water-splitting. Electrochemical kinetics (current density) will have a direct bearing on system cost. We estimate that current densities of about 200 mA/cm² or more are required for a practical cell, although this value is strongly dependent on the cost of electrode materials. Therefore, our rough performance goals were 200 mA/cm² at 0.5 V.

The choice of the best sulfuric acid concentration is not straightforward due to multiple, often opposite, effects. Our experiments with acid concentrations between 1 and 50 weight percent sulfuric acid indicate the following:

- Cathode performance is best at high acid concentrations.
- Anode performance increases markedly as acid concentration is reduced from 50 to 33 weight percent and is relatively insensitive to further reductions in concentration.
- Electrolyte resistivity, which will be directly proportional to cell IR losses, is at a minimum at sulfuric acid concentrations of about 30 to 35 weight percent.

Considering all of these factors, (anode performance and solution resistivity appear most critical), we conclude that sulfuric acid concentrations of 30 to 35 weight percent are preferred, and selected 33 weight percent as the common basis for further experiments.

Temperature effects are relatively straightforward. All other factors being equal, both anode and cathode performances increased across the temperature range investigated (0° to 75°C). However, at a SO₂ pressure at 1 atm over the anolyte, SO₂ solubility decreases with increasing temperature. In some experiments, the reduced activity of SO₂ in the anolyte more than compensated for the increase in anode performance from increased temperature. Higher partial pressures of SO₂ at the anode will be necessary at high

temperatures to maintain SO_2 activity. Temperatures of 75°C or higher are preferred.

None of the anode materials tested performed as well as the two platinum-based materials (smooth and platinized platinum). We certainly did not make a comprehensive materials survey, but platinized platinum or smooth platinum gave the best anode kinetics at a given potential of the five materials examined.

Cell performance in relatively dilute sulfuric acid is better than the performance of a similarly designed cell at acid concentrations of 50 weight percent or above. However, even at the best conditions tested in this program (33 weight percent sulfuric acid, 75°C , platinum anode and cathode, anode saturated with sulfur dioxide at 1 atm pressure), we did not achieve the performance goals of 200 mA/cm^2 at 0.5 V or less. Indeed, it appears unlikely that any cell with anode kinetics limited by the dithionic acid intermediate can achieve such goals.

On the other hand, the use of a homogeneous catalyst such as iodine to replace the anode mechanism does hold promise of meeting the above performance goals with cheap (relative to noble metals) anode materials. The limited number of experiments using homogeneous catalysis yielded a current density of 100 mA/cm^2 at an anode potential of 450 mV RHE on crude porous carbon electrodes at 25°C in 33 weight percent acid. This translates to a total voltage of approximately 600 mV in a properly constructed cell. Factors (untested at present) that would tend to increase this measured performance are higher temperatures, higher SO_2 pressures, and more sophisticated graphite anode fabrication. There is every reason to believe that cell performance goals of 200 mA/cm^2 at 0.5 V can be achieved or exceeded on cheap electrode materials with proper cell development.

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